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TRANSACTIONS

Einige Versuche über die Bestimmung der reduzierenden Zucker im Zuckerrohr und im Handelszucker.

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In einer Reihe von Arbeiten (1 bis 7) haben wir einige Methoden zur Zuckerbestimmung in Gegenwart von Saccharose berichtet. Um den Zuckergehalt des Zuckerrohrsaftes oder des Handelszuckers genau zu bestimmen, ist es nötig, noch einige weitere Versuche zur Ergänzung auszuführen.

1. Zur Zuckerbestimmung nach *Bertrand.*

Bei der Bestimmung der Mono- oder Disaccharide wird in den meisten Fällen die Methode von *Bertrand* verwendet. Diese Methode ist aber bei der Zuckerbestimmung in Gegenwart einer grossen Menge Rohrzuckers unbrauchbar. Wir haben in dieser Arbeit zunächst den Einfluss der Saccharose auf die Zuckerbestimmung nach *Bertrand* untersucht. Auf Grund einer Reihe von Versuchen geben wir für die Berechnung der Zuckermengen aus dem gefundenen Kupferwert die folgende Übersicht an (Tabelle I).

Tabelle I.

Kupfer in mg	Rohrzucker in mg				
	0	0,2	0,4	1,0	2,0
	Invertzucker in mg				
2	1,0	—	—	—	—
4	2,0	—	—	—	—
6	3,0	—	—	—	—
8	4,0	—	—	—	—
10	5,9	0,0	—	—	—
12	5,9	1,0	—	—	—
14	6,9	2,0	—	—	—

16	7,9	3,1	—	—	—
18	8,9	4,2	—	—	—
20	9,9	5,3	—	—	—
22	10,8	6,3	1,1	—	—
24	11,8	7,3	2,3	—	—
26	12,8	8,4	3,5	—	—
28	13,8	9,5	4,7	—	—
30	14,8	10,6	5,8	—	—
32	15,8	11,7	6,9	—	—
34	16,8	12,8	8,0	—	—
36	17,8	14,0	9,0	—	—
38	18,8	15,2	10,2	—	—
40	19,8	16,4	11,3	—	—
42	20,8	17,5	12,3	—	—
44	21,8	18,6	13,4	0,8	—
46	22,9	19,7	14,5	2,1	—
48	24,0	20,8	15,6	3,4	—
50	25,1	21,9	16,7	4,7	—
52	26,1	23,0	17,7	6,0	—
54	27,2	24,1	18,8	7,3	—
56	28,3	25,2	19,9	8,6	—
58	29,4	26,3	21,0	9,9	—
60	30,5	27,5	22,1	11,2	—
62	31,5	28,5	23,2	12,5	—
64	32,5	29,6	24,3	13,9	—
66	33,6	30,7	25,4	15,3	—
68	34,7	31,8	26,6	16,7	0,3
70	35,8	36,2	27,8	18,1	1,8
72	36,9	34,0	29,0	19,4	3,3
74	38,0	35,1	30,2	20,7	4,8
76	39,1	36,2	31,4	22,0	6,3
78	40,2	37,3	32,6	23,3	7,8
80	41,3	38,4	33,9	24,7	9,4
82	42,4	39,5	35,2	25,9	10,8
84	43,5	40,6	36,5	27,1	12,2
86	44,6	41,8	37,8	28,3	13,6
88	45,8	43,0	39,1	29,4	15,0
90	47,0	44,2	40,5	30,7	16,5
92	48,1	45,4	41,8	31,9	17,8
94	49,2	46,6	43,1	33,1	19,1
96	50,3	47,8	44,4	34,4	20,5
98	51,5	49,0	45,7	35,7	21,9
100	52,7	50,2	47,1	37,0	23,3
102	—	—	—	38,4	24,6
104	—	—	—	39,8	25,9
106	—	—	—	41,2	27,2
108	—	—	—	42,6	28,5

110	—	—	—	44,1	29,2
112	—	—	—	45,5	31,2
114	—	—	—	46,9	32,6
116	—	—	—	48,3	34,1
118	—	—	—	49,7	35,5
120	—	—	—	51,2	37,1
122	—	—	—	—	39,0
124	—	—	—	—	40,9
126	—	—	—	—	42,9
128	—	—	—	—	44,9
130	—	—	—	—	46,9
132	—	—	—	—	48,9
134	—	—	—	—	50,9

2. Zur Reinigung der zuckerhaltigen Lösung.

Die Zuckerlösung muss vor der Zuckerbestimmung gereinigt werden. Dazu wird gewöhnlich "dry lead" benutzt. Bei der Verwendung einer zu grossen Menge von "dry lead" wird die Lösung trübe. Es ist daher bei der Reinigung der zuckerhaltigen Lösung notwendig, die geeignete Menge des Reagens hinzuzufügen. Die Verschiedenheit der zuzusetzenden Reagensmenge nach dem Reinheitsgrad der Lösung ist aus Tabelle II ersichtlich.

Tabelle II.

	Farbe des Zuckers in Nummer von "Dutch standard"	Geeignete Menge von "dry lead" in g pro 1 cc 26%iger Zuckerlösung		Farbe des Zuckers in Nummer von "Dutch standard"	Geeignete Menge von "dry lead" in g pro 1 cc 26%iger Zuckerlösung
Handelszucker 1	D. S. 15	0,10~0,30	Handelszucker 5	D. S. 21	0,05~0,10
〃 2	D. S. 17	0,10~0,30	〃 6	—	0,05~0,07
〃 3	D. S. 18	0,10~0,30	〃 7	—	0,05~0,07
〃 4	D. S. 20	0,05~0,10	〃 8	—	0,05~1.00

3. Zur Zuckerbestimmung nach *Luff.*

Wir konnten feststellen, dass nach dieser Methode der Reduktionswert für Glucose demjenigen für Fructose gleich ist (Tabelle III).

Tabelle III.

Zugesetzte Zuckermenge in mg	Glucose		Fructose	
	Verbrauchtes 0,1 n Thiosulfat in cc	Gefundene Zuckermenge in mg	Verbrauchtes 0,1 n Thiosulfat in cc	Gefundene Zuckermenge in mg
10	3,04	9,7	3,14	10,0
20	6,27	19,4	6,37	19,7
30	9,60	29,7	9,70	30,0
40	12,84	39,8	12,84	39,8

Nach der *Luff*schen Methode wird die Mischung auf einem Asbestdrahtnetz in 3 Minuten zum Sieden erhitzt und während 5 Minuten im Sieden erhalten. Um zu starke Erhitzung zu vermeiden, haben wir die Mischung im siedenden Wasserbad erhitzt. Dabei wurde gefunden, dass die Reaktion innerhalb 10 bis 20 Minuten beendingt (Tabelle IV) ist.

Tabelle IV.

Erhitzungsdauer in Min.	Thiosulfatverbrauch in cc		Erhitzungsdauer in Min.	Thiosulfatverbrauch in cc	
	Glucose	Fructose		Glucose	Fructose
5	3,97	5,73	20	6,35	6,30
10	6,03	6,30	30	6,35	6,35
15	6,20	6,28			

Unter den Bedingungen dieser Methode wird auch Rohrzucker einigermassen zersetzt. Wie aus Tabelle V ersichtlich ist, ist aber bei der Saccharosemenge unter 5 g die Korrektion für diesen Zucker entbehrlich.

Tabelle V.

Sacharosemenge in g............	5,00	2,50	1,25	0,05
Thiosulfatverbrauch in cc......	0,30	0,15	0,05	0,00

4. Zur Zuckerbestimmung nach *Ofner*.

Aus den Versuchen in Tabelle VI geht hervor, dass bei Glucose, Fructose und Invertzucker 1 cc 0,0323 n Jod immer 1 mg Zucker entspricht.

Tabelle VI.

Zugesetzter Zucker in mg	Verbrauchtes 0,0322 n Jod in cc		
	Glucose	Fructose	Invertzucker
2,5	2,40	2,45	2,45
5,0	4,75	4,95	4,85
7,5	7,40	7,55	7,50
10,5	9,70	10,25	9,95
12,5	12,10	12,70	12,40

Wir haben dann zur zuckerhaltigen Lösung das *Luff*sche Reagens zugesetzt und die Mischung in einem Wasserbad anstatt auf einem Drahtnetz erhitzt (Tabelle VII).

Tabelle VII.

Erhitzungsdauer in Min.	Verbrauchtes 0,0323 n Jod in cc		Erhitzungsdauer in Min.	Verbrauchtes 0,0323 n Jod in cc	
	Glucose	Fructose		Glucose	Fructose
5	1,40	6,30	30	10,40	10,70
10	5,00	10,00	60	10,40	10,70
20	9,70	10,50			

Wenn die Mischung 30 Minuten im siedenden Wasserbad erhitzt wird, so entspricht, wie aus Tabelle VIII ersichtlich, 1 cc 0,0323 n Jod 0,96 mg Zucker.

Tabelle VIII.

Zugesetzter Zucker in mg	1 cc 0,0323 n Jod entspricht		
	mg Glucose	mg Fructose	mg Invertzucker
1,0	1,00	1,00	1,00
2,5	0,96	0,96	0,96
5,0	0,94	0,94	0,94
7,5	0,94	0,93	0,93
10,0	0,96	0,94	0,95
12,5	0,98	0,95	0,97
Mittel	0,97	0,95	0,96

Enthält die zu untersuchende Lösung neben irgendeinem reduzierenden Zucker noch eine grosse Menge Saccharose, so muss man vor des Berechnung des Zuckergehaltes den Jodverbrauch durch Rohrzucker von der verbrauchten Menge Jod abziehen (Tabelle IX).

Tabelle IX.

Saccharose in g	5,0	2,5	1,0	0,5
Jodverbrauch in cc	1,00	0,50	0,20	0,10

Schrifttum.

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ABSTRACTS
from
TRANSACTIONS published in JAPANESE

(Pages refer to the Japanese originals of this volume unless otherwise noted.)

Separation and Identification of Fatty Acids. Part 3.

A New Method of the Preparation of Pure Oleic Acid and Elaidic Acid by Means of the Hydroxamic Acid Method.

(pp. 411∼413)

By Y. Inouye and H. Yukawa.

(Biochemical Laboratory, Department of Agriculture, Kyoto Imperial University;
Received May 27, 1941.)

In previous papers we proposed a convenient method for the separation and identification of saturated and unsaturated fatty acids, rendering to hydroxamic acid derivatives in crystalline forms which had higher melting points than free acids or any other previously proposed derivatives, e. g., *p*-bromophenacyl ester.

In the present work we isolated oleohydroxamic acid (m. p. 61°) in good yield directly from olive oil by the reaction of hydroxylamine hydrochloride in the presence of sodium ethylate, the details of the method being just the same as described in the previous papers for ethyl ester. And then we confirmed that free acids could be quantitatively recovered through refluxing the hydroxamic acid with dilute alcoholic solution of sulphuric acid. Accordingly, we can recommend this method as a preparation method of pure oleic acid from natural oil, without using the ordinary process of bromination and debromination, the distillation under reduced pressure, or salt-solubility method.

The authors prepared also pure elaidohydroxamic acid (m. p. 91) from elaidic acid, which was obtained by elaidinization of the above oleic acid, and recovered pure elaidic acid again by the same process. The elaidohydroxamic acid is soluble in alcohol, acetone, ether, etc., but insoluble in petroleum ether. And of course it gives characteristic reactions with ferric chloride and copper acetate which are generally those of hydroxamic acids.

Zinc Dust Distillation of some Benzene Compounds.

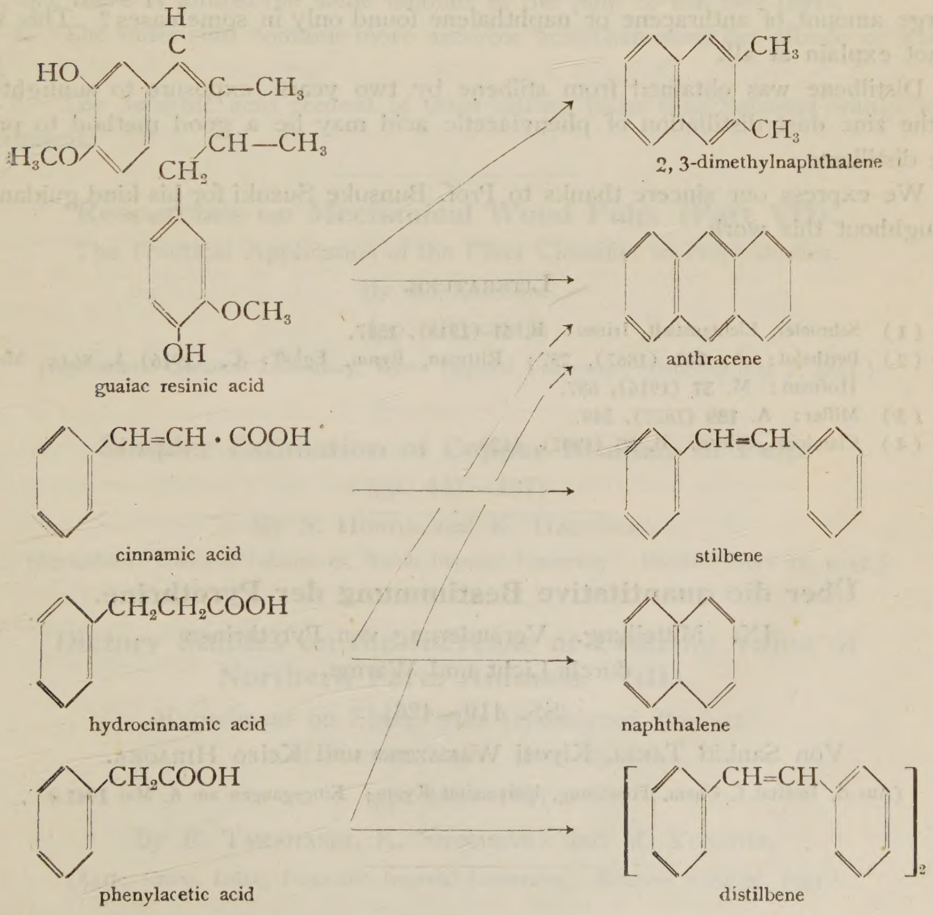
(pp. 414～418)

By Zirô NIKUNI, Hiroshi HAYASHI
and Susumu TSUJI.

(Agricultural Chemical Laboratory, Tokyo Imperial University; Received May 28, 1941.)

We distillated guaiac resinic acid, which was prepared from guaiac resine, with zinc dust in the current of hydrogen gas and obtained 2, 3-dimethylnaphthalene as reported by Schroeter et al⁽¹⁾.

Substrate	Distillate	Crystal	Yield (weight % to substrate)	
guaiac resinic acid 22 g	6.0 g	2, 3-dimethylnaphthalene anthracene	200 mg 60 mg	1 % 0.3 %
cinnamic acid 10 g	3.0 g	stilbene	6 mg	0.06 %
hydrocinnamic acid 10 g	2.67 g	anthracene naphthalene	trace 217 mg	 2 %
phenylacetic acid 20 g	6.1 g	anthracene distilbene	trace 800 mg	 4 %



From the distillate we isolated another crystalline substance, of which on description was found, and decided it to be anthracene.

To explain the mechanism of the formation of anthracene from guaiac resinic acid, we made the zinc dust distillation of some related compounds in the same manner.

First we distillated cinnamic acid with zinc dust, but against our expectations we isolated only a small amount of stilbene. Then hydrocinnamic acid was treated. This time anthracene was obtained in a very small amount, but main crystalline distillate was naphthalene. From phenylacetic acid, we also obtained a small amount of anthracene and an abundance of distilbene.

In each case some about the amount of yellowish oil was obtained besides the crystals, but we could not identify these. The characteristic absorption spectrum of benzene or toluene was not found from these oils.

These results are summarized as follows:

Under such high temperature, anthracene or naphthalene may form from benzene or toluene⁽²⁾, which will be made from the substrate. And stilbene formation by prolonged distillation of cinnamic acid is already reported⁽³⁾. But why was a large amount of anthracene or naphthalene found only in some cases? This we cannot explain at all.

Distilbene was obtained from stilbene by two years' exposure to sunlight⁽⁴⁾. So the zinc dust distillation of phenylacetic acid may be a good method to prepare distilbene.

We express our sincere thanks to Prof. Bunsuke Suzuki for his kind guidance throughhout this work.

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Über die quantitative Bestimmung der Pyrethrine.

IX. Mitteilung. Veränderung von Pyrethrinen durch Licht und Wärme.

(SS. 419～426)

Von Sankiti TAKEI, Kiyosi WAKAZONO und Keizo HIRAOKA.

(Aus d. Institut f. Chem. Forschung, Universität Kyoto; Eingegangen am 6. Mai 1941.)

Ascorbic Acid Content of Citrous Fruits.

(pp. 427～432)

By Yasuo IWASAKI and Toshio KOMATSU.

(Institute for Instruction in Rural Industry, Department of Agriculture and Forestry;
Received May 5, 1941.)

1. The amount of ascorbic acid in Satsuma orange increases according to the ripeness of the fruit. On December 20th the proportion is 38.6 mg/% in the pulp and 212.0 mg/% in the rind. However, the proportion rapidly increases when the orange is changing its color, from the middle to the end of November, both in the pulp and in the rind.

2. The ascorbic acid content in each segment of a given orange is the same. However in rind, there is no marked variation in the individual orange when green (unripened fruit), but there is a conspicuous difference in the early ripening period.

3. In comparing the ascorbic acid content of the upper part of the orange (where the style has been attached) with the lower (where the pedicel has been attached), it is found that there is more ascorbic acid in the rind of the lower part, but there is almost the same amount in the pulp of the two parts.

4. The outer rind contains more ascorbic acid than does the albedo or white rind.

5. The ascorbic acid content of other citrous fruits than Satsuma orange was determined.

Researches on Mechanical Wood Pulp. (Part VII).

The Practical Application of the Fiber Classifier to Pulp-Studies.

By K. KIMURA.

(pp. 433～446)

(Agricultural Chemical Laboratory, Kyoto Imperial University; Received May 7, 1841.)

Simpler Estimation of Copper Number of Pulp.

(pp. 447～457)

By S. HONDA and K. HAGIWARA.

(Agricultural Chemical Laboratory, Kyoto Imperial University; Received April 18, 1941.)

Dietary Studies on the Increase of Utilizing Value of Northern Farm Animals. (III).

Experiment on Sheep with Hydrolyzed Products of Human Hair. (Part 1).

(pp. 458～464)

By E. TAKAHASHI, K. SHIRAHAMA and M. YOSHIDA.

(Agric. Chem. Labo., Hokkaido Imperial University; Received April 26, 1941.)

Studies on Methionine and its Derivatives. (I).

On the Detection of Methionine.

(pp. 465～475)

By Yoshio TSUCHIYA.

(S. Suzuki and Co., Ltd.; Received May 17, 1941.)

The present author has found that methylmercaptan was formed from methionine by alkali-fusion. And when the mercaptan is introduced into the isatin-sulfuric acid (0.01～0.02 g isatin to 100 cc H_2SO_4), the yellow color of the reagent becomes grass green.

Applying this color reaction to the protein hydrolysates, the author has now established the detection method of methionine. The color reaction is not given by cystine, from which sulfretted hydrogen is produced under the same experimental conditions. In this case, the yellow color of the reagent becomes first a light rose and then gradually diminishes and finally a dilute milky turbidity is produced.

Sulfuretted hydrogen, on the contrary, inhibits this reaction.

Therefore, when both methionine and cystine are present in the same sample, like protein hydrolysates, the gas produced must be introduced after the sulfuretted hydrogen is separated from the gas mixture of CH_3SH and H_2S, by passing it through the powdered lead acetate tube.

Of the naturally occurring amino acids, methionine only gives this reaction. No perceptible color change of the reagent is observed by the other amino acids such as glycine, alanine, valine, leucine, phenylalanine, tyrosine, proline, aspartic acid, glutamic acid, lysine, arginine, and histidine. And also, neither the mixture of the amino acids except methionine, especially that of cystine and the others, nor that of cystine and carbohydrates such as glucose, maltose, lactose, levurose, and sucrose, gives this reaction. In other words, methylmercaptan is not produced from these mixtures under this procedure.

While the same color change as methionine is observed in the case of employing the mixture of cystine and betaine, and also in the case of employing the compounds containing methylmercapto group such as γ-methylmercapto-α-oxybutylic acid, γ-methylmercapto-propyl-amine, and γ-methylmercapto-propyl-alcohol (methionol), the oxidative derivatives of methionine such as methionine sulfoxide, β-methylsulfone-propionic acid, and homocystine, from which sulfuretted hydrogen is produced like cystine, cause no color changes in the reagent. Accordingly, it is clear that the color reaction of isatin-sulfuric acid reagent was characteristic for methylmercapto group.

The sensibility of this detection method is very sharp, i. e., this reaction is positive even in the case of employing 0.2 mg of methionine.

When this method is applied to the protein hydrolysates, cystine can also be detected at the same time as methionine, by ascertaining the formation of black lead sulfide from lead acetate.

Care must especially be taken that the excess of water is entirely removed from the sample before experiment. Otherwise sulfuretted hydrogen is also formed from methionine by the secondary decomposition of methylmercaptan in the presence of alkali and water, thus causing the diminution of the sensibility of the detection of methionine itself, as well as mistake in judgement of the detection of cystine.

The common procedure of this detection method of methionine (as well as cystine) is as follows :—0.2∼100 mg of the dried sample and 3∼5 drops of KOH or NaOH (0.45∼0.75 g) are taken in the test tube (ca. 20 cc) and fused in the flame of burner for 1∼2 minutes. After the fused mass thus obtained is acidified with dilute sulfuric or hydrochloric acid, the gas mixture of CH_3SH and H_2S now liberated is passed first through the lead acetate tube and then through the isatin-sulfuric acid by means of aeration.

Thus the author has ascertained that, considering from this detection method, the comparative contents of methionine and cystine in several proteins such as egg albumin, casein, hemoglobin, edestine, gelatine, soybean protein, gluten, silk and wool, were identical with those found quantitatively, which had been hitherto reported in literature.

On the Chemical Studies of the Bagasse Pulp. (4).

(pp. 476∼478)

By Tetutaro TADOKORO, Masao NISHIDA and Keizō ITŌ.

(Hokkaido Imperial University; Received May 15, 1941.)

Researches on Bamboo in Taiwan as a Raw Material for Pulp. Part V.

(On the Digestion of "Keitiku" by the Magnesium Sulfite Method).

(pp. 479∼482)

By Minoru TUTIYA, Setuo FUKUHARA and Yoshiteru KATO.

(Industrial Research Institute of Taitu; Received May 5, 1941.)

It is absolutely necessary for the pulp making of bamboo (or Gramineae) by sulfite method for a little or the same quantity of sulfite to be present in the cooking liquid, i.e., its constitution is $Mg(HSO_3)_2+MgSO_3$. Otherwise we cannot obtain the pulp, because at the temperature of 145∼150°C, the chip becomes black by sulfuric acid from sulfurous acid. Owing to this, bamboo cannot be digested by Ca-sulfite liquid at these temperatures. Excess of free acid is fatal to the pulp making of the bamboo. Using a liquid which was in very slight excess of $MgSO_3$, we obtained pulp but it was not good in quality and yield. Our experiments were undertaken at maximum temperatures of 145°C and 150°C. When cooked at lower temperature such as 100°C (80 hrs.), 130°C (2 hrs., to elevate to 130°C spending 8 hrs.), using Ca-sulfite liquid, we obtained pulp. But these methods would not be applicable for commercial purposes.

We arrived at the following conclutions :—

1. We obtained light coloured and bleachable pulp from "Keitiku" by $MgSO_3$ process, as well managed as by the Ca-sulfite method, in respect to the temperature and hours.

2. For bamboo pulp making Ca-sulfite process is not suitable for commercial purposes. The constitution of the cooking liquid must be $Mg(HSO_3)_2 + MgSO_3$, and a small quantity of soluble $MgSO_3$ is absolutely necessary.

3. The best conditions are as follows :—

Total SO_2 is more than 4%. Insufficient quantity of SO_2 induces failure.

Maximum temperature is 145~150°C (5 hrs.) and total cooking hours is 8 hours.

4. The pulps were rich in ash and pentosan, and the values of Cu-index were a little high. These characteristics are not agreable for artificial silk or staple fibre, but may be used for paper making.

5. The pulps obtained by maximum temperature of 145°C were good in physical characters, but bad in the contents of non-cellulose matters, and by 150°C were bad in physical characters but good in non-cellulose contents.

6. The pulp for artificial silk or staple fibre cannot be obtained from bamboo by single cooking of sulfite method for commercial purposes.

On the Flavonol Glucoside of Euphorbia thymifolia L.

(pp. 483~484)

By Makoto Nagase.

(Agricultural Chemical Department, Taihoku Imperial University Taiwan;
Received May 16, 1941.)

The leaves and stems of Euphorbia thymifolia L. were extracted with ethanol and the solvent was evaporated in vacuum. The aqueous solution of the residue was extracted with acetic ester. From the concentrated extract a flavon glucoside was isolated (yield 0.037 %) which formed yellow needles (mp. 203~203°) from aceton and had the formula $C_{21}H_{20}O_{10} + 2H_2O$. On hydrolysis with dilute H_2SO_4, the glucoside gave one molecule of apigenin (tri actate mp. 182°) and glucose (phenyl-osazone mp. 201°).

When the glucoside was mixed with 5, 7, 4′-trioxyflavon-7-glucoside, obtained from apiin by E. v. Gerichten's method, the melting point was not depressed.

Thus the isolated glucoside was proved to be 5, 7, 4′-trioxyflavon-7-glucoside.

Functional Studies on Soil (XXIII~XXVI).

(pp. 485~490)

By Hideo Misu,

(Agricultural Experiment Station, Government General of Tyosen; Received May 13, 1941.)